

⑪ Ⓐ No. 1013960

④⑤ ISSUED 770719

⑤② CLASS 71-7.0
C.R. CL.

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CANADIAN PATENT

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HERBICIDAL COMPOSITION FOR GRASSY AND
BROADLEAF WEEDS

⑦⑩

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APPLICATION No. 160,333

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FILED 730102

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PRIORITY DATE U.S.A. (233,818) 720310

No. OF CLAIMS 13 - No drawing

This invention is in the chemical arts. It pertains to that branch of chemistry having to do with chemical ways and means for the control of weeds.

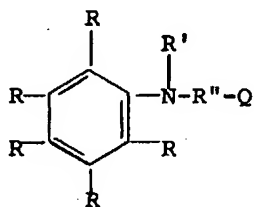
Recently, certain N-substituted N-phenylamines have been found which at practical concentrations have both pre- and post-emergence toxicity to grassy weeds. Moreover, at concentrations at which these new N-substituted N-phenylamines kill or prevent growth of grassy weeds a number of crop plants are relatively unaffected by them. On the other hand, broadleaf weeds in general appear to have a greater tolerance to these compounds at these concentrations. Consequently, when these N-substituted N-phenylamines are used, other herbicides that kill or prevent growth of broadleaf weeds without substantially reducing the effect of the N-substituted N-phenylamines on grassy weeds and without combining with the N-substituted N-phenylamines to cause substantial kill or reduction in the growth of crop plants must be used when it is desired to kill or prevent the growth of both kinds of weeds in crops.

A problem to which this invention provides a solution is to find herbicides meeting the above requirements.

In summary, this invention provides a process and a composition of matter.

The inventive process, in brief, comprises applying at about the same time to the habitat of both broadleaf and grassy weeds (1) an effective quantity of certain N-substituted N-phenylamine material, and (2) an effective quantity of complementary compound selected from the group consisting of norea, fluometuron, chloroxuron, diuron, linuron, fenuron, atrazine and pyrazon.

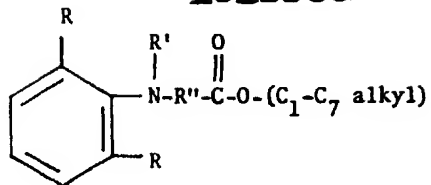
The N-substituted N-phenylamine material of this invention is selected from the group of N-phenylamines represented by the formula:



in which each R is selected from the group consisting of hydrogen, halo, nitro, trihalomethyl, C₁-C₇ alkyl and C₁-C₇ alkoxy, R' is selected from the group consisting of hydrogen and mono-, di- and trihaloacetyls, R'' is selected from the group consisting of C₁-C₇ alkylene and C₂-C₇ alkylidene, and Q is selected from the group consisting of carboxyl, and salts and C₁-C₇ alkanol esters thereof, amide, mono- and di-substituted amides in which the substituents are selected from the group consisting of C₁-C₇ alkyl and aryl, carbonylhydrazide, and 1-substituted carbonylhydrazides in which the substituents are selected from the group consisting of C₁-C₇ alkyl and aryl. In these definitions, C₁-C₇ alkyl includes both straight and branched chain alkyls, examples of which include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, and the like. C₁-C₇ alkoxy encompasses both straight and branched chain alkoxys having 1-7 carbon atoms, examples of which include methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, t-butoxy, pentoxy and the like. Halo includes fluoro, chloro, bromo and iodo. C₁-C₇ alkylene comprises both straight and branched chain alkenes having 1-7 carbon atoms, examples of which include ethylene, propylene, 1-methylethylene, 2-methylethylene, butylene, 1-methylpropylene, 2-methylpropylene, 3-methylpropylene, 1,1-dimethylethylene, 1,2-dimethylethylene, 2,2-dimethylethylene, and the like. C₂-C₇ alkylidene comprises both straight and branched chain alkylidenes having 2-7 carbon atoms, such as, for example, ethylidene, propylidene, isopropylidene, butylidene, 1-methylpropylidene, 2-methylpropylidene, and the like. Examples of salts include ammonium salt, alkali metal salts (sodium, potassium, and the like), alkali earth metal salts (calcium, magnesium, and the like) and amine salts (methylamine, diethylamine, tripropylamine, diphenylamine, and the like). Examples of C₁-C₇ alkanol esters include the methyl ester, ethyl ester, the propyl ester, the isopropyl ester and the like. Aryl includes phenyl, tolyl, naphthyl, and the like.

In a preferred form of the invention, the N-substituted N-phenylamine is selected from the group of compounds represented by the formula:

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in which each R is $\text{C}_1\text{--C}_7$ alkyl, R' is selected from the group consisting of mono-, di- and trihaloacetyl, and R'' is selected from the group consisting of $\text{C}_1\text{--C}_7$ alkylene and $\text{C}_2\text{--C}_7$ alkylidene and the complementary compound is hyrazon;

Examples of compounds covered by the generic formula are:

N-(p-chlorophenyl)glycine ethyl ester
N-(m-chlorophenyl)glycine ethyl ester
N-(o-chlorophenyl)glycine ethyl ester

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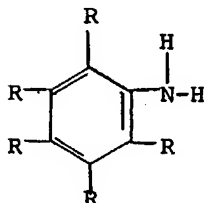
- N-phenylglycine ethyl ester
 N-(2,3-dichlorophenyl)glycine ethyl ester
 N-(3,4-dichlorophenyl)glycine ethyl ester
 N-(2-chloro-4-nitrophenyl)glycine ethyl ester
 N-(4-chloro-3-nitrophenyl)glycine ethyl ester
 N-(2,4,5-trichlorophenyl)glycine ethyl ester
 N-chloroacetyl-N-(p-chlorophenyl)glycine ethyl ester
 N-chloroacetyl-N-(m-chlorophenyl)glycine ethyl ester
 N-chloroacetyl-N-(o-chlorophenyl)glycine ethyl ester
 10 N-chloroacetyl-N-phenylglycine ethyl ester
 N-chloroacetyl-N-(2,3-dichlorophenyl)glycine ethyl ester
 N-chloroacetyl-N-(3,4-dichlorophenyl)glycine ethyl ester
 N-dichloroacetyl-N-(p-chlorophenyl)glycine ethyl ester
 N-dichloroacetyl-N-(m-chlorophenyl)glycine ethyl ester
 N-dichloroacetyl-N-(o-chlorophenyl)glycine ethyl ester
 N-dichloroacetyl-N-phenylglycine ethyl ester
 N-dichloroacetyl-N-(2,3-dichlorophenyl)glycine ethyl ester
 N-dichloroacetyl-N-(3,4-dichlorophenyl)glycine ethyl ester
 N-trichloroacetyl-N-(p-chlorophenyl)glycine ethyl ester
 20 N-trichloroacetyl-N-(m-chlorophenyl)glycine ethyl ester
 N-trichloroacetyl-N-(o-chlorophenyl)glycine ethyl ester
 N-trichloroacetyl-N-phenylglycine ethyl ester
 N-trichloroacetyl-N-(2,3-dichlorophenyl)glycine ethyl ester
 N-trichloroacetyl-N-(3,4-dichlorophenyl)glycine ethyl ester
 N-chloroacetyl-N-(2-chloro-4-nitrophenyl)glycine ethyl ester
 N-chloroacetyl-N-(4-chloro-3-nitrophenyl)glycine ethyl ester
 N-chloroacetyl-N-(2,4,5-trichlorophenyl)glycine ethyl ester
 N-dichloroacetyl-N-(2-chloro-4-nitrophenyl)glycine ethyl ester
 N-dichloroacetyl-N-(4-chloro-3-nitrophenyl)glycine ethyl ester
 30 N-dichloroacetyl-N-(2,4,5-trichlorophenyl)glycine ethyl ester
 N-trichloroacetyl-N-(2-chloro-4-nitrophenyl)glycine ethyl ester
 N-trichloroacetyl-N-(4-chloro-3-nitrophenyl)glycine ethyl ester
 N-trichloroacetyl-N-(2,4,5-trichlorophenyl)glycine ethyl ester
 N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester
 N-chloroacetyl-N-(3-chloro-2-methoxyphenyl)glycine ethyl ester
 N-dichloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester
 N-dichloroacetyl-N-(3-chloro-2-methoxyphenyl)glycine ethyl ester
 N-trichloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester
 N-trichloroacetyl-N-(3-chloro-2-methoxyphenyl)glycine ethyl ester
 40 N-(2,6-dichlorophenyl)glycine ethyl ester
 N-(4-chloro-2,6-dinitrophenyl)glycine ethyl ester
 N-(2,6-dichloro-4-nitrophenyl)glycine ethyl ester
 N-chloroacetyl-N-(2,6-dichlorophenyl)glycine ethyl ester
 N-dichloroacetyl-N-(2,6-dichlorophenyl)glycine ethyl ester
 N-trichloroacetyl-N-(2,6-dichlorophenyl)glycine ethyl ester
 N-chloroacetyl-N-(4-chloro-2,6-dinitrophenyl)glycine ethyl ester
 N-trichloroacetyl-N-(4-chloro-2,6-dinitrophenyl)glycine ethyl ester
 N-chloroacetyl-N-(2,6-dichloro-4-nitrophenyl)glycine ethyl ester
 N-dichloroacetyl-N-(2,6-dichloro-4-nitrophenyl)glycine ethyl ester
 50 N-trichloroacetyl-N-(2,6-dichloro-4-nitrophenyl)glycine ethyl ester
 N-(2,4-dichlorophenyl)glycine ethyl ester
 N-chloroacetyl-N-(2,4-dichlorophenyl)glycine ethyl ester
 N-dichloroacetyl-N-(2,4-dichlorophenyl)glycine ethyl ester
 N-trichloroacetyl-N-(2,4-dichlorophenyl)glycine ethyl ester
 N-(2,6-diethylphenyl)glycine ethyl ester
 N-chloroacetyl-N-phenylalanine
 N-bromoacetyl-N-phenylalanine
 4-(N-chloroacetyl anilino)butyramide
 60 α-(N-chloroacetyl-2',6'-diethylanilino)acetylhydrazine
 4-(N-trichloroacetyl-2',6'-dichloroanilino)butyric acid sodium salt
 4-(N-trichloroacetyl-3',4'-dichloroanilino)crotyric acid
 2-[4-(2',4'-dichloroanilino)butyryl]-1-phenylhydrazine
 N-chloroacetyl-N-(2',4',5'-trichlorophenyl)alanine
 4-(N-trichloroacetyl anilino)butyric acid ammonium salt
 N-chloroacetyl-N-(m-trifluoromethylphenyl)glycine ethyl ester
 N-trichloroacetyl-N-(m-trifluoromethylphenyl)alanine ethyl ester

- N-(p-trifluormethylphenyl)glycine
 N-chloroacetyl-N-(2,6-diethylphenyl)alanine ethyl ester
 N-carbethoxyethyl-N-chloroacetyl-2,6-diethylalanine
 N-chloroacetyl-N-(2-methyl-6-ethylphenyl)alanine ethyl ester
 N-carbethoxyethyl-N-chloroacetyl-2-methyl-6-ethylaniline
 N-chloroacetyl-N-(2,6-dimethylphenyl)glycine
 N-chloroacetyl-N-(2,6-dimethylphenyl)glycine sodium salt
 N-chloroacetyl-N-(2,6-dimethylphenyl)glycine ammonium salt
 N-chloroacetyl-N-(2,6-dimethylphenyl)glycine ethyl ester
 10 N-chloroacetyl-N-(2,6-diethylphenyl)glycine
 N-chloroacetyl-N-(2,6-diethylphenyl)glycine sodium salt
 N-chloroacetyl-N-(2,6-diethylphenyl)glycine ammonium salt
 N-chloroacetyl-N-(2-methyl-6-ethylphenyl)glycine
 N-chloroacetyl-N-(2-methyl-6-ethylphenyl)glycine sodium salt
 N-chloroacetyl-N-(2-methyl-6-ethylphenyl)glycine ammonium salt
 N-chloroacetyl-N-(2-methyl-6-ethylphenyl)glycine ethyl ester
 N-chloroacetyl-N-(2-chloro-6-methylphenyl)glycine
 N-chloroacetyl-N-(2-chloro-6-methylphenyl)glycine sodium salt
 N-chloroacetyl-N-(2-chloro-6-methylphenyl)glycine ammonium salt
 20 N-chloroacetyl-N-(2-chloro-6-methylphenyl)glycine ethyl ester
 N-bromoacetyl-N-(2,6-diethylphenyl)glycine
 N-bromoacetyl-N-(2,6-diethylphenyl)glycine sodium salt
 N-bromoacetyl-N-(2,6-diethylphenyl)glycine ammonium salt
 N-bromoacetyl-N-(2,6-diethylphenyl)glycine ethyl ester

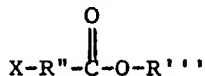
The compounds represented by the formula range in color
 from brown to yellow and in state at 20-25°C. from liquid to solid.
 In general, the esters of this invention are insoluble in water, but
 in solvents such as acetone and the like, and such as benzene and
 the like, they are soluble to the extent suitable for herbicidal
 30 uses. On the other hand, in general the inventive acids, salts, a-
 mides and hydrazides are soluble in water at least to the extent
 suitable for herbicidal uses. These compounds are characterized by
 both pre- and post-emergence toxicity to a number of grassy weeds.
 On the other hand, at concentrations at which these N-phenylamines
 are not tolerated by such weeds, a number of desirable crop plants
 are relatively unaffected by these compounds.

These N-phenylamines can be made by reacting in a liquid
 reaction medium containing a base such as potassium hydroxide or the
 like the corresponding phenylamine:

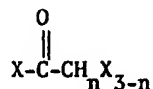
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with a haloalkanoic acid or ester of the formula:



in which X is halo, to form the compounds of the class in which R' is hydrogen. These compounds are reacted with mono-, di- and tri-haloacetylhalides of the formula:



in which n is 0-2, to form the remaining N-phenylamines of this invention.

Norea is the common name for 3-(3a,4,5,6,7,7a-hexahydro-4,7-methanoindan-5-yl)-1,1-dimethyl urea. This compound and its preparation are disclosed in the U.S. Patent, No. 3,304,167, to Buntin et al.

Fluometuron is the common name for N-3-trifluoromethylphenyl -N',
10 N'-dimethyl urea. This compound and its preparation are disclosed in the U.S. Patent, No. 3,134,665, to Martin et al. It is commercially available under the trademark Cotoran.

Chloroxuron is the common name for 3-[p(p-chlorophenoxy)phenyl]-1,1-dimethyl urea. This compound and a process for making it are disclosed in the U.S. Patent, No. 3,060,235, to Martin et al. It is commercially available under the trademark Tenoran.

Diuron is the common name for 3-(3,4-dichlorophenyl)-1,1-dimethyl urea. This compound and its preparation are disclosed in the U.S. Patent, No. 2,655,445, to Todd. It is commercially available under the trademark Karmex.

20 Linuron is the common name for 3-(3,4-dichlorophenyl)-1-methoxy-1-methyl urea. This compound and its preparation are disclosed in the U.S. Patent No. 2,960,534, to Scherer et al. It is commercially available under the trademark Lorox.

Fenuron is the common name for 3-phenyl-1,1-dimethyl urea. This compound and a process for making it are disclosed in the U.S. Patent, No. 2,655,447, to Todd. It is commercially available under the trademark Dybar.

Atrazine is the common name for 2-chloro-4-ethylamino-6-isopropylamine-s-triazine. This compound can be made by the reaction of cyanuric chloride with a molecular portion of ethylamine at

-15-0°C. to form 2,4-dichloro-6-diethylamino-s-triazine which in turn is reacted with a molecular portion of isopropylamine to form atrazine. See the U.S. Patent, No. 2,891,855, to Gysin et al. Atrazine is commercially available.

B Pyrazon is the common name for 5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone. This compound and its synthesis are disclosed in the U.S. Patent, No. 3,222,159, to Reicheneder et al. It is commercially available under the ^{trademark} ~~name~~ Pyramin.

The quantities of N-phenylamine material and complementary compound applied to the habitat of broadleaf and grassy weeds in general depend upon local conditions, the kinds of broadleaf and grassy weeds that are prevalent, and, when a crop is involved, tolerance of the crop to the N-phenylamine material and the complementary compound. In general, an application rate of about 1/7 - 5 pounds per acre for the N-phenylamine material and for the compound with a weight ratio of the complementary compound to the N-phenylamine material of about 4:1-1:12 gives satisfactory results. However, lower and higher application rates and weight ratios are within the broader concepts of this invention. In this connection, most, if not all, of the combinations of N-phenylamine material and complementary compound of this invention appear to synergistically affect one or more weed species. Consequently, as to a synergistically affected grassy weed, for example, to achieve a 100% kill or 100% no growth of that weed, the rates of application of the N-phenylamine material and of the complementary compound to the habitat of that weed can be significantly lower than in the case where only N-phenylamine material or complementary compound are applied to the habitat of that weed.

The N-phenylamine material and the complementary compound of this invention are applied at about the same time to weed habitats by conventional ways and means. In some embodiments of the process, they are applied separately on the same day or within a week of each other. In preferred embodiments of the process they are applied

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simultaneously as a mixture.

The composition of matter of this invention comprises a phytotoxic mixture consisting essentially of an effective quantity of N-phenylamine material of this invention and an effective quantity of a complementary compound of this invention. In some embodiments the composition comprises only the mixture. In other embodiments, the dispersible embodiments, the composition comprises an effective quantity of the mixture, and application aid material.

The dispersible embodiments of the composition of this invention range from concentrates of the phytotoxic mixture to the ultimate use composition that is applied in the field. Accordingly, an effective concentration of the phytotoxic mixture in the composition of this invention is in a broad range, generally being from about 0.1 to about 90% by weight of the composition. Higher and lower concentrations, however, are within the broader concepts of this invention. In concentrate embodiments, the concentration of the phytotoxic mixture generally is in a range from about 10 to about 90% by weight of the composition and preferably in a range from about 10 to about 50% by weight of the composition. In the ultimate use embodiments, the concentration generally is in a range from about 0.1 to about 20% by weight of the composition and preferably in a range from about 0.5 to about 10% by weight of the composition.

Application aid material is generally inert material that facilitates distribution or dispersion of the phytotoxic mixture when it is applied to soil or to foliage of undesirable plants. It encompasses diluents, carriers, extenders, surfactants, spreading agents, sticking agents, wind drift control agents, and the like.

In these dispersible embodiments of the herbicidal composition of this invention, which are normally solid, the application aid material is generally an inert solid in a divided condition.

Some embodiments of the solid dispersible composition are granular, while others are dispersible powders or dusts.

The granular compositions are of the coated type, the impregnated type or the incorporated type.

The coated type of granular composition is made by dusting a wettable powder or ground powder of the phytotoxic mixture onto granular carrier material which either before or after the dusting has been admixed with a sticker. Water, oils, alcohols, glycols, aqueous gums, waxes and the like, including mixtures thereof, are used as stickers. Examples of granular carrier material include attaclay, corn cobs, vermiculite, walnut hulls and almost any granular mineral or organic material screened to the desired size. Generally the phytotoxic mixture is about 2-20% by weight of the granular composition, the sticker is generally about 5-40% by weight of the composition and the granular carrier material is generally about 60-93% by weight of the composition.

In the case of the impregnated type of granular composition, the phytotoxic mixture is dissolved in a solvent or melted, and then sprayed on or poured into the granular carrier material. The solvent can be removed by evaporation, or permitted to remain. In either case, the phytotoxic mixture impregnates the particles of the granular carrier material. Examples of the granular carrier material include those just mentioned with respect to the coated type of granular composition. The phytotoxic mixture is generally about 2-20% by weight of the composition, while the granular carrier material is generally about 80-98% by weight of the composition.

Relative to the incorporated type of granular composition, the phytotoxic mixture is mixed with an inert finely divided solid such as, for example, clay, carbon, plaster of paris, and the like, and made into a mud with water or other inert evaporable liquid. The mud is then dried to a solid sheet or cake, broken up or comminuted, and screened to the desired particle size. In other embodiments, the mud is put into a granular pan and granules are formed therein with subsequent removal of the water or solvent. In still another procedure, the mud is extruded through a die into rods which are cut into small pieces. In the incorporated type of granular composition, the phytotoxic mixture generally is about 2-50% by weight of the composition, and the solid carrier material is about 50-98%

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by weight of the composition.

In all granular embodiments of the dispersible herbicidal compositions of this invention, various additives in minor concentrations relative to the carrier material also can be present.

In the other embodiments of the dispersible solid herbicidal compositions of this invention, the carrier is usually a dispersible inert solid. A typical dispersible solid of this type is clay. Other suitable dispersible solids include talc, attapulgite, pyrophyllite, diatomaceous earth, kaolin, aluminum magnesium silicate, montmorillonite, Fullers earth, sawdust and the like. The solid dispersible compositions can be air dispersible, in which case they can be applied as dusts. They can be water dispersible, in which case they are usually referred to as wettable powders. Generally when it is intended that the composition be water dispersible, the composition preferably contains emulsifying material (one or more surfactants) at concentration sufficient to enable a suspension of the desired degree of stability to be formed when the composition is admixed with a suitable quantity of water. A typical dispersible solid composition of this invention generally comprises about 10-80% by weight of phytotoxic mixture, about 20-90% by weight of solid carrier material, and, when emulsifying material is present, about 1-10% by weight of emulsifying material.

Other specific embodiments of the herbicidal composition of this invention comprise solutions of the phytotoxic mixture of this invention in inert, preferably volatile, solvents for the phytotoxic mixture. Such a solution, which can be regarded as a concentrate, typically comprises about 10-50% by weight of phytotoxic mixture and about 50-90% by weight of solvent. The solution can be applied as is, or diluted with more solvent and applied, or, when one or more components of the phytotoxic mixture are water-insoluble, dispersed in water or water dispersed in it, and applied. Preferably, when it is intended that the solution of water-insoluble components be dispersed in water or water be dispersed in it, the mixture of solution and water also comprises emulsifying material at

a concentration sufficient to enable a dispersion of the desired degree of stability to be formed. A typical emulsifying material concentration is about 1-10% by weight of the concentrate. The water concentration is such that the phytotoxic mixture concentration is about 0.5-10% by weight of the total composition.

Examples of the surfactants employed in both the liquid and solid compositions of this invention comprise the well-known surface active agents of the anionic, cationic or nonionic types and include alkali metal (sodium or potassium) oleates and similar soaps, amine salts of long chain fatty acids (oleates), sulfonated animal and vegetable oils (fish oils and castor oil), sulfonated petroleum oils, sulfonated acyclic hydrocarbons, sodium salts of lignin sulfonic acids, alkyl naphthalene sodium sulfonates, sodium lauryl sulfonate, disodium monolauryl phosphates, sorbitol laurate, pentaerythritol monostearate, glycerol monostearate, polyethylene oxides, ethylene oxide condensates of stearic acid, stearyl alcohol, stearyl amine, rosin amines, dehydroabietyl amine and the like, lauryl amine salts, dehydroabietyl amine salts, lauryl pyridinium bromide, stearyl trimethylammonium bromide, and cetyl dimethylbenzylammonium chloride.

Still other examples are listed in "Detergents and Emulsifiers - 1968 Annual" by John W. McCutcheon.

In addition to the phytotoxic mixture and application aid material, some specific embodiments of the dispersible herbicidal composition of this invention comprise one or more other components, examples of which include plant growth regulators, insecticides, acaricides, fungicides, nematocides, plant nutrients, and the like.

The dispersible herbicidal composition of this invention is used by applying it by conventional ways and means to soil and to foliage of weeds.

The rate of application of the composition of this invention is such as to provide an effective concentration of the phytotoxic mixture in the soil, on the weed foliage, or both in the soil and on the foliage, depending on the method of application and what is desired.

The best mode now contemplated of carrying out this invention is illustrated by the following working examples of various aspects of this invention, including specific embodiments. This invention is not limited to these specific embodiments. In these examples all percentages are by weight unless otherwise indicated, all parts by weight are indicated by "w", all parts by volume are indicated by "v", and each part by weight (w) bears the same relationship to each part by volume (v) as the kilogram does to the liter.

Example 1

10 This example illustrates a specific embodiment of a process for making N-(2,6-diethylphenyl)glycine ethyl ester, an N-substituted N-phenylamine of this invention.

 Ethyl bromoacetate (480 w) is added dropwise to a stirred mixture of 2,6-diethylaniline (429 w), potassium hydroxide (161 w) and dimethylformamide (1500 v). During the addition of ethyl bromoacetate, the temperature of the reaction mixture typically rises slightly. After addition is complete, the mixture is stirred at 90-110°C. for one hour. During this period of time the potassium hydroxide dissolves and a white precipitate slowly forms. The reaction mixture is cooled to 20-25°C., poured into water (2000 v) and
20 extracted with diethyl ether (700 v) three times. The ether extracts are combined, washed with water, an aqueous solution of hydrochloric acid (10%), an aqueous solution of sodium bicarbonate (5%), and water, and then dried. The diethyl ether is removed by evaporation under reduced pressure. The residue (426.8 is typically a red oil. It consists essentially of N-(2,6-diethylphenyl)glycine ethyl ester.

 In similar fashion the other N-phenylamines of this invention in which R' is H are made from the corresponding anilines and haloalkanoic acids or esters.

30

Example 2

 This example illustrates a specific embodiment of a process for making N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester, another N-substituted N-phenylamine of this invention.

 To a stirred solution of 2,6-diethylphenylglycine ethyl

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ester (531.5 w), made as in Example 1, in benzene (2.5 v) is added dropwise chloroacetyl chloride (306 w) followed by pyridine (196 w). During the additions the temperature of the reaction mixture typically rises from 20-25°C. to about 70°C. After the additions are complete, the resulting reaction mixture is stirred at 70-80°C. for 3 hours, cooled to 20-25°C., and filtered. The filtrate is washed with the water, an aqueous solution of hydrochloric acid (10%), an aqueous solution of sodium bicarbonate (5%), and water, and then dried. The benzene is removed by evaporation under reduced pressure.

10 The residue (711.0 w), the desired product, is typically a red oil which crystallizes on standing. A typical analysis of the product is: N = 4.4%, Cl = 11.9%; (calculated: N = 4.4%, Cl = 11.3%). The product consists essentially of N-chloroacetyl-(2,6-diethylphenyl) glycine ethyl ester.

In similar fashion the other N-phenylamines of this invention in which R' is mono-, di and tri-haloacetyl are made from the corresponding compounds of this invention in which R' is H, and the corresponding mono-, di- and tri-haloacetyl halides.

Examples 3-9

20 These examples illustrate specific embodiments of the dispersible herbicidal composition of this invention.

The general formulation of these embodiments is:

<u>Components</u>	<u>Concentration</u>
Phytotoxic mixture	1 w
Poly(oxyethylene) sorbitan monolaurate in which the average oxyethylene content is 20 mole %	1 v
Toluene	1 v

30 The components of the phytotoxic mixture in each example, relative weight ratio of the components, the crop or crops in which each specific composition is particularly useful, time of application (Pre = preemergence; Post = postemergence), and suggested rates of application, based on the phytotoxic mixture, are set forth in the following Table I.

Each embodiment of the composition of the foregoing formulation is made by admixing the components at 20-25°C. The result

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in each instance is a water emulsifiable concentrate.

This emulsifiable concentrate is used by admixing it with water to give an emulsion containing the phytotoxic mixture at whatever concentration is desired, and the emulsion is sprayed over the area to be treated at a rate selected to give the desired rate of application of the phytotoxic mixture.

Ex.No.	Components of Phytotoxic Mixture Example 2 Product	Weight Ratio of Components 1:2-2:1	TABLE I		Rate of Application (lbs. per acre)
			Crops	Time of Appln.	
3	Example 2 Product Norea	1:2-2:1	Barley	Pre	3/4 - 4
			Corn Cotton Peanuts Sorghum Soybeans Peas Snap beans Wheat	Weeds Downeybrome grass Foxtail grass Pigweed Wild Oats Rye Grass Carpetweed Barnyard grass Crabgrass Mustard Coffee Weed Velvet Leaf Spurge Purslane	
4	Example 2 Product Fluometuron	1:1.2	Cotton Peas Peanuts	Pre	2.2
5	Example 2 Product Chloroxuron	1:1 - 2:1	Soybeans	Post	2-3
			(Early when grasses have 1-2 leaves & height of 1 inch)	Crabgrass Green Foxtail Barnyard grass Pigweed Mustard	

Ex.No.	Components of Phytotoxic Mixture	Weight Ratio of Components	TABLE I (Cont'd)		Rate of Application (lbs. per acre)
			Crops	Time of Appln.	
6	Example 2 Product Diuron	2:1 - 1:2	Wheat Cotton Soybeans Corn	Pre	3/4 - 2
7	Example 2 Product Linuron	2:1 - 1:2	Wheat Cotton Soybeans Corn	Pre	Wild oats
					Crabgrass
					Barnyard grass
					Pigweed
					Lambs Quarter
					Rye grass
					Downeybrome grass
					Teaweed
					Velvet leaf
					Curled mustard
					Coffee weed
					Jimson weed
	Example 2 Product Fenuron	0.4:1 - 1.2:1	Corn Cotton Soybeans	Pre	Foxtail
					Rye grass
					Downeybrome grass
					Crabgrass
					Foxtail
					Barnyard grass
					Teaweed
					Velvet leaf
					Pigweed
					Lambs quarter
					Curled mustard
					Morning Glory
8	Example 2 Product Atrazine	12:1 - 1:1	Corn Sorghum	Post	German Millet
					Crabgrass
					Green Foxtail
					Barnyard grass
					Pigweed
					Mustard
					Crabgrass
					Green Foxtail
					Barnyard grass
					Pigweed
					Mustard
					Jimson weed
9	Example 2 Product Pyrazon	1:1 - 1:4	Peas Red beets Sugar beets		Velvet leaf
					Rag weed

Typical results obtained in the practice of this invention are exemplified by the following tabulated data which are the best data so far obtained in the actual testing of various embodiments of a composition of this invention. These data were obtained in standard greenhouse tests and in field tests. The results of these tests are in most instances expressed as % reduction in growth in the case of the preemergence tests, and % kill or injury in the case of post-emergence tests. In all of these tests the results were determined by comparing treated areas with untreated control areas in the pre-

10 emergence tests, and treated plants with untreated control plants in the postemergence tests. In the following tables the legend "lb/A.-a.i." means pounds of active agent per acre.

Synergism was deemed to be present when the observed result was substantially greater than the expected result which was calculated according to the equation:

$$E = x + y - \frac{xy}{100}$$

in which x is the % reduction of growth or % kill or injury by herbicide A at p pounds per acre, y is the % reduction of growth or % kill or injury by herbicide B at q pounds per acre, and E is the

20 expected % reduction of growth or % kill or injury by herbicides A and B at p + q pounds per acre. The basis and logic of this equation are discussed in Weeds, 15, pages 20-22.

Table II presents preemergence data obtained in field tests of N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester, norea, fluometuron, mixtures of the ester and norea, and mixtures of the ester and fluometuron.

TABLE II

Phytotoxic Material (lb/A.a.i.)	Rate	Foxtail	Barnyard grass	Crabgrass	Wild oats	Average grasses	Mustard	Coffee weed	Velvet leaf	Teaweed	An. Morning Glory	Pigweed	Spurge	Cocklebur	Purslane	Average Broadleaf	Cucumber	Alfalfa	Peanuts	Sweet peas	Wheat	Snap beans	Rice	Cotton	Soybeans	Sorghum	Corn	Sugar beets
N-Chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	1.0	94	99	99	65	89	7	7	12	0	5	95	71	5	90	32	10	0	4	5	5	0	25	5	0	4	5	0
	2.0	99	100	100	72	93	6	7	20	7	2	100	89	7	100	38	30	10	7	11	11	1	41	0	0	24	0	6
Norea	1.5	70	71	97	62	75	77	66	85	0	25	91	74	12	100	59	82	77	2	12	31	5	54	7	0	0	4	80
Ester + Norea	1.0 + 1.5	99	99	100	90*	97	90*	70	90	30*	4	100	95	32	100	68	75	76	0	7	30	30	74	0	14	4	11	90
	2.0 + 1.5	96	100	100	90*	96	88*	33	73	38*	15	99	92	32	100	63	60	75	2	10	45	27	68	1	2	19	7	98
Fluometuron	1.2	87	75	97	90	87	100	94	92	100	75	100	97	19	100	86	97	100	50	26	55	82	82	6	37	26	10	100
Ester + Fluometuron	1.0 + 1.2	100	97	100	95	98	100	99	96	100	81	100	99	22	100	89	77	100	26	22	65	83	89	11	49	45	40	100

*Synergistic result

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Table III presents preemergence data obtained in greenhouse tests of N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester, norea and mixtures of the two relative to weed control and wheat tolerance.

TABLE III

Phytotoxic Material	Rate lb/A.a.i.	% Weed Control						% Wheat Injury
		Curled Mustard	German Millet	Barnyard Grass	Corn Cockle	Downeybrome Grass	Wild Oats	
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	0.5	0	97	97	0	35	80	0
Norea	0.5	0	45	80	0	10	35	16
	1.0	60	97	100	15	60	70	38
Ester + Norea	0.5 + 0.5	40*	100	97	45*	85*	90	16
	0.5 + 1.0	95*	100	100	45*	97*	100	0

*Synergistic result

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Table IV presents preemergence data obtained in greenhouse tests of N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester, norea, diuron, linuron, mixtures of the ester and diuron, and mixtures of the ester and linuron on ryegrass and downeybrome grass.

TABLE IV

Phytotoxic Material	Rate lb/A.a.i.	% Control	
		Ryegrass	Downeybrome
10 N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester	3/8	0	10
	3/4	70	82
Norea	3/8	50	43
	3/4	80	90
Ester + Norea	3/8 + 3/8	80*	58*
	3/4 + 3/8	98*	72
	3/8 + 3/4	93*	90
	3/4 + 3/4	95	75
Diuron	3/8	20	15
	3/4	85	28
20 Ester + Diuron	3/8 + 3/8	17	33*
	3/4 + 3/8	83	70
	3/8 + 3/4	57	75*
	3/4 + 3/4	93	80
Linuron	3/8	0	3
	3/4	20	20
Ester + Linuron	3/8 + 3/8	57*	55*
	3/4 + 3/8	87*	62
	3/8 + 3/4	63*	72*
	3/4 + 3/4	85*	60

*Synergistic result

30 Table V presents data obtained in postemergence field tests in soybeans of N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester, chloroxuron, and mixtures of these two compounds. In this table EP stands for early postemergence application, that is, when grasses have 1-2 leaves and are 1 inch tall, while P stands for postemergence application when grasses have 3-4 leaves and are 2-3 inches tall.

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TABLE V

Phytotoxic Material	Rate lb/A.a.i.	Time of Application	% Weed Control					% Soybean Injury
			Crab- grass	Green Foxtail	Barnyard Grass	Pigweed	Mustard	
N-chloroacetyl-N- (2,6-diethylphenyl) glycine ethyl ester	1.0	EP	25	25	0	18	0	0
	2.0		38	62	72	30	0	0
Chloroxuron	1.0	EP	60	92	85	100	100	35
	2.0		96	94	97	99	100	80
Ester + Chloroxuron	1.0 + 1.0	EP	80*	88	80	100	100	25
	2.0 + 1.0		98*	90	98	100	100	48
Ester	1.0	P	0	10	28	35	18	0
	2.0	P	30	5	42	75	0	0
Chloroxuron	1.0	P	42	45	55	100	98	65
	2.0		82	58	52	100	100	42
Ester + Chloroxuron	1.0 + 1.0	P	62*	75*	78*	100	100	48
	2.0 + 1.0		82*	78*	85*	100	100	48

*Synergistic Result

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Tables VI and VII set forth greenhouse data obtained in the preemergence testing of N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester, linuron and mixtures of these two compounds. These data are based on a scale of 0-10 with 0 being no kill or injury or inhibition of growth and 10 being 100% kill or injury or inhibition of growth.

TABLE VI

Phytotoxic Material	Rate lb/A.a.i.	Barnyard Grass	Crab- grass	Morning Glory	Tea- weed	Velvet Leaf	Mari- golds	Curled Mustard	Coffee- weed	Jimson Weed	Sorghum	Soy- beans	Cotton
N-chloroacetyl-N- (2,6-diethylphenyl) glycine ethyl ester	3/8	10	8	0	6	0	4	0	2	2	3	0	2
Linuron	3/8 3/4	3 8	3 10	1 5	1 10	10 10	2 6	10 10	10 10	7 10	1 0	0 0	0 2
Ester + Linuron	3/8 + 3/8 3/8 + 3/4	10 10	9 10	0 1	8* 10	10 10	3 4	10 10	8 10	7 8	6 9	0 0	2 2

*Synergistic result

TABLE VII

Phytotoxic Material	Rate lb./A.a.i.	Soy- beans	Cotton	Sorghum	Corn	Morning Glory	Tea- weed	Pig- weed	Barnyard Grass	Foxtail	Velvet Leaf	Curled Mustard	Wild Oats
N-chloroacetyl-N- (2,6-diethylphenyl) glycine ethyl ester	1/2	0	3.0	5.5	2.0	0	5.0	8.5	10.0	9.5	4.0	2.5	3.5
Linuron	1/4 1/2	2.5 0	4.0 0	2.5 1.5	0 0	0 0	3.0 10.0	10.0 10.0	0 3.0	5.0 7.0	7.0 10.0	0 8.0	0 1.5
Ester + Linuron	1/2 + 1/4 1/2 + 1/2	5.5 0	2.5 1.0	7.5 5.0	0 1.5	1.5 1.5	1.5 9.5	10.0 10.0	10.0 10.0	10.0 10.0	6.5 9.5	7.0 8.5	10.0* 9.0*

*Synergistic result

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Table VIII reports greenhouse data obtained in preemergence testing of N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester, diuron, linuron, mixtures of the ester and diuron, and mixtures of the ester and linuron. These data are reported on a scale of 0-10 with 0 being no kill, injury or inhibition of growth and 10 being 100% kill, injury or inhibition of growth.

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TABLE VIII

Phytotoxic Material	Rate lb/A.a.i.	Wheat	Wild Oats	Downey- brome	Crab- grass	Barnyard Grass	Pigeon weed	Lambs- quarter	Alfalfa	Cotton	Soy- beans	Sugar beets
N-chloroacetyl-N- (2,6-diethylphenyl) glycine ethyl ester	1/2	0	9	4	10	10	5	3	5	0	0	0
Diuron	1/4	3	4	2	5	0	10	7	3	0	0	6
	1/2	5	5	1	10	5	10	10	4	0	0	8
Ester + Diuron	1/2 + 1/4	0	10	5	10	10	10	10*	10*	0	-	7
	1/2 + 1/2	0	10	3	10	10	10	10*	10*	0	2	8
Linuron	1/4	0	0	3	9	0	9	10	5	0	0	7
	1/2	0	0	1	9	5	10	10	10	0	3	8
Ester + Linuron	1/2 + 1/4	3	10	0	10	10	10	10	10*	0	3	9
	1/2 + 1/2	3	9	5	10	10	10	10	10	0	0	9

*Synergistic result

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Table IX gives greenhouse data obtained in the preemergence testing of N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester, fenuron, and mixtures of these two compounds. The data in this table are based on a scale of 0-10 with 0 being no injury or kill or inhibition of growth, and 10 being 100% injury or kill or inhibition of growth.

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TABLE IX

Phytotoxic Material	Rate lb/A.s.i.	Corn	Cotton	Soy- beans	Crab- grass	Fox- tail	Barnyard Grass	Tea- weed	Velvet leaf	Pig- weed	Lambs- quarter	Curled Mustard	Morning Glory
N-chloroacetyl-N- (2,6-diethylphenyl) glycine ethyl ester	3/8	0	0	0	7	10	9	1	0	8	0	0	0
Fenuron	0.15	0	0	0	1	1	2	8	10	9	9	10	6
	0.30	0	0	3	6	5	6	10	10	9+	10	9+	8
	0.45	2	1	4	7	6	6	9	10	10	9+	10	8
Ester + Fenuron	3/8 + 0.15	0	0	3	8	10	9+	8	10	10	9+	10	1
	3/8 + 0.30	3	1	2	9	10	9+	10	10	10	9+	10	8
	3/8 + 0.45	4	1	6	10	10	9+	10	10	10	9+	10	9

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In Table X are summarized postemergence data obtained in the greenhouse testing of N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester, atrazine and mixtures of the two compounds for the control of German Millet.

TABLE X

<u>Phytotoxic Material</u>	<u>Rate (lb/A.a.i.)</u>	<u>Test #1</u>	<u>Test #2</u>
N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester	1/2 3/4	20 61	26 38
10 Atrazine	1/16 1/8	18 74	19 50
Ester + Atrazine	1/2 + 1/16 3/4 + 1/16 1/2 + 1/8 3/4 + 1/8	75* 83* 85* 88	79* 77* 90* 95*

*Synergistic result

In Table XI are set forth postemergence data obtained in field testing N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester, atrazine and mixtures of these two compounds for weed control in grain sorghum. In the table EP means early postemergence application when the grasses have 1-2 leaves and are 1 inch tall, while P represents postemergence application when the grasses have 3-4 leaves and are 2-3 inches tall.

TABLE XI

Phytotoxic Material	Rate (lb/A.a.i.)	Time of Application	% Weed Control				% Sorghum Injury
			Crab- grass	Green Foxtail	Barnyard Grass	Pigweed	Mustard
N-chloroacetyl-N- (2,6-diethylphenyl) glycine ethyl ester	1.0	EP	25	25	0	18	0
	2.0		38	62	72	30	0
Atrazine	1.0	EP	48	85	68	100	100
Ester + Atrazine	1.0 + 1.0	EP	90*	99*	98*	100	100
	2.0 + 1.0	EP	100*	99*	100*	100	100
Ester	1.0	P	0	10	28	35	18
	2.0	P	30	5	42	75	0
Atrazine	0.5	P	65	42	48	100	100
	1.0	P	85	82	80	100	100
Ester + Atrazine	1.0 + 0.5	P	88*	82*	62	100	100
	2.0 + 0.5	P	92*	88*	96*	100	99
	1.0 + 1.0	P	84	65	90*	100	100
	2.0 + 1.0	P	98*	98*	99*	100	100

*Synergistic result

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Table XII presents results of preemergence field testing of N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester, pyrazon and mixtures of the two compounds for weed control in peas and red beets.

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TABLE XII

Phytotoxic Material	Rate lb/A.a.i.	% Weed Control				% Crop Injury	
		Annual Grasses	Lambs. quarter	Jimson Weed	Velvet Leaf	Rag- weed	Pig- weed
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	1.0	98	0	0	-	0	95
	2.0	100	20	0	-	0	100
Pyrazon	2.0	75	100	67	100	100	98
	4.0	87	100	98	100	100	100
Ester + Pyrazon	1.0 + 2.0	52	85	-	0	58	100
	1.0 + 4.0	96	98	100	100	100	100
	2.0 + 2.0	94	88	100	100	100	100
						Peas	Red Beets
						0	0
						0	13
						0	27
						13	10
						5	10
						35	37
						37	20

*Synergistic result

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Table XIII contains data obtained in the field testing of N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester, pyrazon and mixtures of the two compounds for weed control in sugar beets. In the table "Pre" means preemergence application and "Post" means postemergence application.

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TABLE XIII

Phytotoxic Material	Rate lb/A.a.i.	Time of Application	% Weed Control			% Injury Sugar beets
			Lambs- quarter	Rag- weed	Annual Grasses	
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	1.0	Pre	25	0	99	0
	2.0	Pre	12	0	100	0
	4.0		0	0	100	0
Pyrazon	4.0	Pre	99	100	99	0
Ester + Pyrazon	1.0 + 4.0	Pre	97	100	99	3
	2.0 + 4.0	Pre	98	96	99	5
Ester	1.0	Post	7	0	100	0
	2.0	Post	0	0	100	0
	4.0	Post	0	0	100	0
Pyrazon	4.0	Post	88	100	86	0
Ester + Pyrazon	2.0 + 2.0	Post	98	100	100	0
	2.0 + 4.0	Post	98*	100	100	0

*Synergistic result

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From the data of the foregoing tables it can be seen that the various embodiments of the phytotoxic material of this invention are effective against a number of both grassy weeds and broadleaf weeds, while being tolerated by a number of crops. Moreover, in many instances these embodiments have synergistic phytotoxic effects on a variety of weeds.

Hence, this invention provides a new and useful herbicidal composition and a new and useful process for controlling weeds.

Other features, advantages and specific embodiments of
10 this invention will become readily apparent to those exercising ordinary skill in the art after reading the foregoing disclosures. Such specific embodiments are within the scope of the claimed subject matter unless expressly indicated to the contrary by claim language. Moreover, while specific embodiments of this invention have been described in considerable detail, variations and modifications of them can be effected without departing from the spirit and scope of the invention as disclosed and claimed.

The expression "consisting essentially of" as used in
20 this specification excludes any unrecited substance at a concentration sufficient to substantially adversely affect the essential properties and characteristics of the composition of matter being defined, while permitting the presence of one or more unrecited substances at concentrations insufficient to substantially adversely affect said essential properties and characteristics.

**HERBICIDAL COMPOSITION FOR
GRASSY AND BROADLEAF WEEDS**

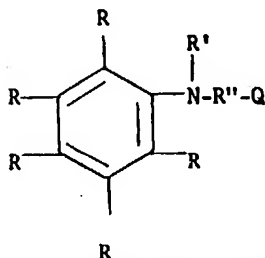
Abstract of Disclosures

Disclosed are a process and a composition for killing both grassy and broadleaf weeds in a number of valuable crops. The process comprises applying to the habitat of these weeds at about the same time effective quantities of certain N-substituted N-phenylamine material and a complementary compound selected from the group consisting of norea, fluometuron, chlormuron, diuron, linuron, fenuron, atrazine and pyrazon. The composition comprises a mixture of the N-phenylamine material and the complementary compound. The mixture is synergistically phytotoxic relative to various weeds.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the control of grassy and broadleaf weeds, which comprises applying to the habitat of said weeds at about the same time effective quantities of (1) N-substituted N-phenylamine material selected from the group of N-phenylamines represented by the formula:



in which each R is selected from the group consisting of hydrogen, halo, nitro, trihalomethyl, C₁-C₇ alkyl and C₁-C₇ alkoxy, R' is selected from the group consisting of hydrogen and mono-, di- and trihaloacetyls, R'' is selected from the group consisting of C₁-C₇ alkylene and C₂-C₇ alkylidene, and Q is selected from the group consisting of carboxyl, and salts and C₁-C₇ alkanol esters thereof, amide, mono- and di-substituted amides in which the substituents are selected from the group consisting of C₁-C₇ alkyl and aryl, carbohydrazide, and 1-substituted carbohydrazides in which the substituents are selected from the group consisting of C₁-C₇ alkyl and aryl, and (2) a compound selected from the group consisting of norea, fluometuron, chloroxuron, diuron, linuron, fenuron, atrazine and pyrazon, the quantities of (1) and (2) so applied being such that at least one of said weeds is synergistically controlled by (1) and (2).

2. A process according to claim 1 in which said N-phenyl-amine material consists essentially of N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester.

3. A process according to claim 2 in which the weight ratio of the compound to N-phenylamine material is in a range from about 4:1 to about 1:12.

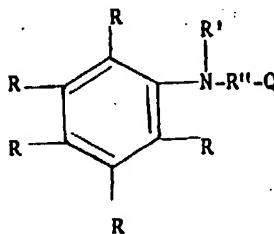
4. A process according to claim 3 in which each of said quantities is about 1/7 - 5 pounds per acre.

5. A process according to claim 4 in which said habitat is land planted with a crop.

6. A process according to claim 1, 2 or 3 in which said complementary compound is norea.

7. A process according to claim 1, 2 or 3 in which said complementary material consists essentially of pyrazon.

8. A herbicidal composition useful for the control of grassy and broadleaf weeds, which comprises (A) an effective quantity of a mixture that is synergistic to at least one of said weeds and that consists essentially of (1) N-substituted N-phenylamine material selected from the group of compounds represented by the formula:



in which each R is selected from the group consisting of hydrogen, halo, nitro, trihalomethyl, C_1-C_7 alkyl and C_1-C_7 alkoxy, R' is selected from the group consisting of hydrogen and mono-, di- and trihaloacetyls, R'' is selected from the group consisting of C_1-C_7 alkylene and C_2-C_7 alkylidene, and Q is selected from the group consisting of carboxyl, and salts and C_1-C_7 alkanol esters thereof, amide, mono- and di-substituted amides in which the substituents are selected from the group consisting of C_1-C_7 alkyl and aryl, carbonylhydrazide, and 1-substituted carbonylhydrazides in which the substituents are selected from the group consisting of C_1-C_7 alkyl and aryl, and (2) a complementary compound selected from the group consisting of norea, fluometuron, chloroxuron, diuron, linuron, fenuron, atrazine and pyrazon, the weight ratio of the compound to the N-phenylamine material is in a range from about 4:1 to about 1:12 and (B) application aid material.

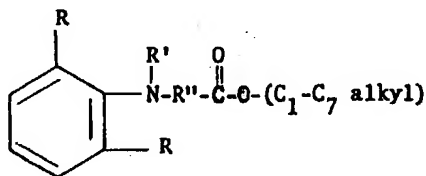
9. A herbicidal composition according to claim 8 in which said N-phenyl-

amine material consists essentially of N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester.

10. A herbicidal composition according to claim 8 or 9 in which said complementary compound is norea.

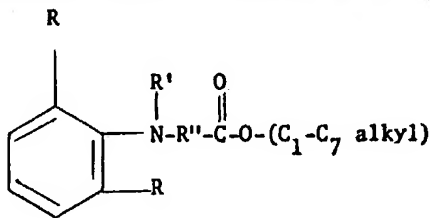
11. A herbicidal composition according to claim 8 or 9 in which said complementary material is pyrazon.

12. A process for the control of grassy and broadleaf weeds, which comprises applying to the habitat of said weeds at about the same time and prior to emergence of said weeds effective quantities of (1) N-substituted N-phenylamine material selected from the group of N-phenylamines represented by the formula:



in which each R is $\text{C}_1\text{--C}_7$ alkyl, R' is selected from the group consisting of mono-, di- and trihaloacetyl, and R'' is selected from the group consisting of $\text{C}_1\text{--C}_7$ alkylene and $\text{C}_2\text{--C}_7$ alkylidene, and (2) pyrazon, the quantities of (1) and (2) so applied being such that at least one of said weeds is synergistically controlled by (1) and (2).

13. A herbicidal composition useful for the preemergence control of grassy and broadleaf weeds, which comprises (A) and effective quantity of a synergistic mixture consisting essentially of (1) N-substituted N-phenylamine material selected from the group of compounds represented by the formula:



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in which each R is C₁-C₇ alkyl, R' is selected from the group consisting of mono-, di- and trihaloacetyl, and R'' is selected from the group consisting of C₁-C₇ alkylene and C₂-C₇ alkylidene, and (2) pyrazon, the weight ratio of pyrazon to the N-phenylamine material being in a range from about 4:1 to about 1:12, and (B) application aid material.

